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Apatite- and Wollastonite-Containg Glass-Ceramics for Prosthetic Application

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Glass powders −350 mesh of the composition MgO 4.6, CaO 44.9, SiO_2 34.2, P_2O_5 16.3, CaF_2 0.5 in weight ratio were compacted, heated up to 1050°C at a rate of 5°C/min and held at 1050°C for 2 h. The resultant glass-ceramic had a high density of 99.3% and contained a fairly large amount of oxy- and fluoro-apatite and wollastonite crystals. It showed high bending and compressive strengths of 157 and 1060 MPa, respectively. Pieces of the glass-ceramic implanted in rabbits formed tight bond with their bones within 8 weeks.

KEY WORDS: Implant/ Biocompatibility/ Bond between implant and bone/ Mechanical strength/ Crystallization of glass/ MgO-CaO-SiO_2-P_2O_5/

I. INTRODUCTION

Metals and plastics have been used primarily as implant materials for bone and joint replacement for a long time. Recently, much attention has been paid on ceramics because of their good compatibility with living tissues. Among them, alumina ceramics are already used practically. They show high mechanical strengths and good biocompatibility. However, they do not create a strong chemical bond with the bones, and hence, must be fixed within the body by a mechanical interlocking with the bones. Such interlocking, however, is liable to become loose for long period. Glass[1] and glass-ceramics[2] containing CaO and P_2O_5 as well as hydroxyapatite ceramics[3] were reported to create a strong chemical bond with the bones. Their mechanical strengths[2,4~7] hitherto reported, are however, low, and hence they are practically seldom used.

The present authors have found that the glass-ceramics containing apatite and wollastonite crystals have high mechanical strengths and also are capable of forming strong chemical bond with bones. The method of their preparation and their physical and biological properties are described.

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II. EXPERIMENTAL

1. Preparation of Glass

Six compositions in the pseudo-ternary system $3CaO \cdot P_2O_5$–$CaO \cdot SiO_2$–$MgO \cdot CaO \cdot 2SiO_2$ shown in Fig. 1 and four compositions derived from one of them by adding various amounts of CaF_2 were examined. Their nominal compositions on the basis of weight ratio are given in Table I.

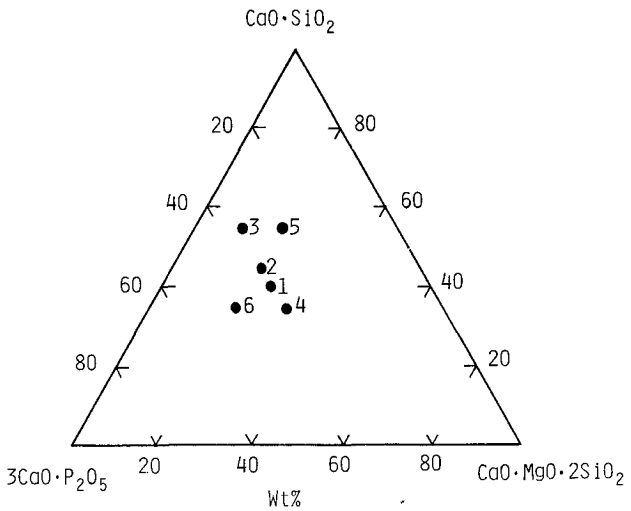

Fig. 1. Compositions investigated in the system $3CaO \cdot P_2O_5$–$CaO \cdot SiO_2$–$CaO \cdot MgO \cdot 2SiO_2$.

Table I. Nominal composition of glasses (weight ratio)

Composition	MgO	CaO	SiO_2	P_2O_5	CaF_2
1	4.6	44.9	34.2	16.3	0.00
2	3.7	45.9	34.4	16.0	0.00
3	1.9	48.1	34.0	16.0	0.00
4	5.6	43.6	34.8	16.0	0.00
5	3.7	45.3	39.6	11.4	0.00
6	3.7	46.5	29.2	20.6	0.00
1+0.25F	4.6	44.9	34.2	16.3	0.25
1+0.50F	4.6	44.9	34.2	16.3	0.50
1+0.75F	4.6	44.9	34.2	16.3	0.75
1+1.00F	4.6	44.9	34.2	16.3	1.00

Batch mixtures yielding about 30 g melts of these compositions were prepared from reagent grade chemicals of MgO, $CaCO_3$, SiO_2, $CaHPO_5 \cdot 2H_2O$ and CaF_2. They were put into a Pt10%Rh crucible of 50 ml capacity, calcined at 1000°C for 10 h and then melted at 1450°C for 2 h in a SiC furnace. The melts were poured onto a steel plate and pressed into plates approximately 2 mm thick.

2. Crystallization of Glass

A preliminary experiment showed that when the glass plates as-prepared were heat-treated, fibrous crystals grew from the glass surface and shrinkage cavities were formed in the center of the crystallized products.

In order to prevent the formation of the long crystals and big cavities, the glass plates as-prepared from the melts were pulverized to − 350 mesh (44 μm opening) using a sintered alumina ball mill (Spex Industries Inc., Model 8000-II). The powders thus obtained were mixed with water in 10/1 weight ratio and pressed into discs 40 mm in diameter by 15 mm thick at 400 kg/cm^2. The powder compacts were placed on a sintered alumina plate, heated up to 1050°C at a rate of 5°C/min and held at 1050°C for 2 h in a SiC furnace. Then the electric current to the furnace was cut off and heat-treated specimens were allowed to cool in the furnace.

3. Thermal Analysis

About 0.13 g of the glass powders prepared as described in section 2 were put into a platinum cell and subjected to differential thermal analysis (DTA) with a thermoanalyzer (Shimadzu Seisakusho Ltd., Model DT-30). The heating rate was 5°C/min.

Cubic pieces $7 \times 7 \times 7$ mm cut from the green glass powder compacts prepared as described in section 2 were subjected to thermal shrinkage measurement. The thermoanalyzer described above was used. The heating rate was 5°C/min.

Lectangular pieces $7 \times 6 \times 15$ mm cut from the glass powder compact previously heat-treated as described in section 2 were subjected to thermal expansion measurements. The thermoanalyzer described above was also used. The measurements were made in the temperature range from room temperature to 980°C at a heating rate of 10°C/min.

4. X-Ray Diffraction Analysis

Glass powders were heated to the various temperatures corresponding to the respective exothermal peaks on the DTA curve, and subjected to X-ray diffraction analyses to identify the crystalline phases precipitated.

The glass powder compacts previously heat-treated as described in section 2 were also subjected to powder X-ray diffraction analyses to identify the crystalline phases precipitated.

5. Measurement of Porosity

The glass powder compacts previously heat-treated were polished with CeO_2 powders and observed under a metallurgical microscope to measure the relative volume of pores.

Cubic pieces $10 \times 10 \times 10$ mm were cut from the glass powder compacts previously heat-treated and their bulk densities were measured using Archimedean technique. Their true densities were measured by a pycnometer method after they were powdered −350 mesh. Pure water was used as the immersion liquid in both the measurements. The true porosities were calculated from the bulk and true densities.

6. Measurement of Mechanical Property

6.1. Young's Modulus

The discs of the glass powder compacts previously heat-treated were ground with #2000 alumina powders. Propagation velosities, V_l and V_t, of 650 MHz longitudinal and transverse sound waves were measured in the direction perpendicular to the plane surface of the discs by a pulse transmission method. The Young's moduli, E, of the specimens were calculated from these velosities and bulk densities ρ measured by the method described in section 5 using the following equation.[8)]

$$E=\frac{\rho V_t^2(3V_l^2-4V_t^2)}{(V_l^2-V_t^2)} \quad (1)$$

6.2. Vickers Hardness

The plane surfaces of the discs of the glass powder compacts previously heat-treated were polished with CeO_2 powders. Their Vickers hardness were measured with a small hardness tester (Ernst Leits Co., Durimet) using an indenter with a 50 g load. Ten measurements were made on each of the samples.

6.3. Bending Strength

Bars $5\times5\times20$ mm were cut from the glass powder compacts previously heat-treated and the surface of the bars were ground with #2000 alumina powders. They were subjected to three-point bending tests at a cross-head speed of 0.5 mm/min using a Instron-type testing machine (Shimazu Seisakusho Ltd., Autograph Model DSS-500). Their bending strengths σ_f were calculated from the equation

$$\sigma_f=\frac{3}{2}\frac{Pl}{t^3} \quad (2)$$

where P is the load necessary to cause fracture, l the distance between the two supporting knife edges (16 mm in the present experiment) and t the thickness of the specimen. Five measurements were made for each of the samples.

6.4. Compressive Strength

Cubic pieces $4\times4\times4$ mm were cut from the glass powder compacts previously heat-treated, ground with #2000 alumina powders, and polished with CeO_2 powders. The specimens were placed between two steel blocks, the surfaces of which were lubricated with a colloidal MoS_2-dispersed paste, and subjected to the measurements of the compressive strengths using a Instron-type testing machine (Shimazu Seisakusho Ltd., Universal Testing Machine Model RS-2). The cross-head speed was 0.65 mm/min. Nine measurements were made for each of the samples.

6.5. Study of Biological Property

Plates $10\times15\times2$ mm were cut from the glass powder compacts previously heat-treated, ground with #1500 emery papers and cleaned with ethanol in an ultrasonic cleaner for 20 min. They were implanted into condyles of tibae of male rabbits weighing 3.0 to 3.5 kg as schematically shown in Fig. 2(A). For comparison, sintered dense alumina ceramic (Bioceram®) and sintered dense hydroxyapatite ceramic, kindly served by Kyocera Co. and Mitsubishi Mining Co., respectively, and Hench's Bioglass 45S5[1)] (Na_2O 24.5, CaO 24.5, SiO_2 45.0, P_2O_5 6.0 in wt %) prepared in the present authors' laboratory were also implanted in the same way.

The portions of the tibae containing the implants were excised various weeks

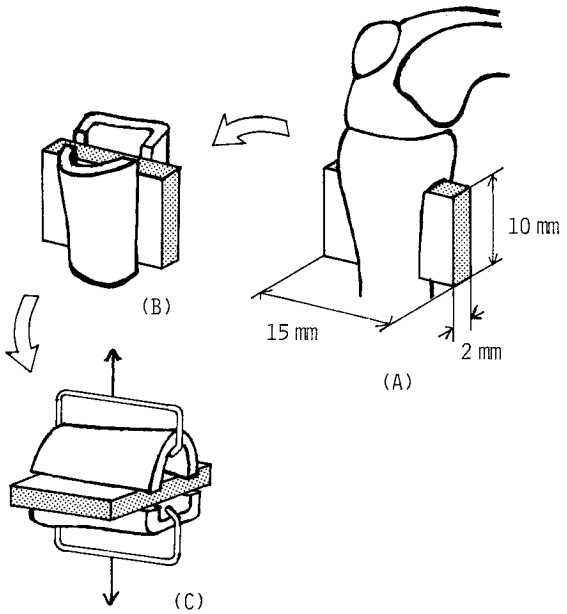

Fig. 2. Procedure for testing bond between implant and bone.

after the operation. Some of them were cut perpendicularly to the interface between the implant and the bone and thinned, and the thin sections were observed with a contact radiomicrography to study the biocompatibility of the implant.

The others were subjected to the measurement of the strength of the bond between the implant and the bone: The bones located at the lateral sides of the implants were removed by a dental bar, as shown in Fig. 2(B). Each bone located at the both plane surfaces of the implant were hoocked and pulled in a opposite direction, as shown in Fig. 2(C). The loads at which fracture occurred were measured using a Instron-type testing machine (Shimazu Seisakusho Ltd., Autograph Model S-500). The cross-head speed was 5 mm/min. The contact area between the implant and the bone was approximately 45 mm^2. The numbers of the measurements were 5, 4, 8 and 4 for the present glass-ceramic, alumina ceramic, hydroxyapatite ceramic and Bioglass, respectively.

III. RESULT AND DISCUSSION

1. Microstructure of Glass-Ceramics

The crystalline phases identified in the heat-treated glass powder compacts as well as the relative volumes of the pores determined in the compacts are given in Table II. As an example, the pores observed in the heat-treated specimen of the composition 1+0.50F is shown in Fig. 3. The relative volume of the pores as observed in this specimen was represented by single open circle in Table II. The more open circles represent the more pores present in the specimens.

Table II shows that the glass powder compact of the composition 1+0.50F can be transformed by the heat treatment without deformation into a dense glass-

Table II. Microstructure of glass-ceramics

Composition	*Crystalline phase**	*Pores***	*Remarks*
1	(Ap) W (CP)	○○○	
2	(Ap) W (CP)	○○○	
3	(Ap) W (CP)	○○○	
4	(Ap) W (CP)	○○○	
5	(Ap) W (CP)	○○○	deformed
6	Ap (W)	○○○○	
1+0.25F	Ap W	○○	
1+0.50F	Ap W	○	
1+0.75F	Ap W	○○	
1+1.00F	Ap W	○○	

* Ap: Oxy- or fluoro-apatite ($Ca_{10}(PO_4)_6(O, F_2)$), W: β-Wollastonite (β-$CaO \cdot SiO_2$), CP: Whitlockite (β-$3CaO \cdot P_2O_5$), ( ): In small amount.

** Measure of total volume of pores (○→○○○○ indicates increase in total volume).

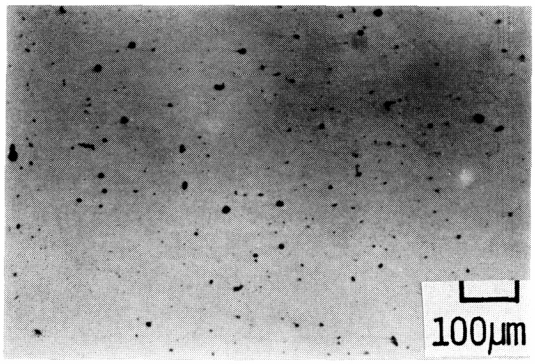

Fig. 3. Pores in the glass powder compact of the composition 1+0.50F heat-treated.

ceramic containing a fairly large amount of both apatite ($Ca_{10}(PO_4)_6(O, F_2)$) and β-wollastonite ($CaO \cdot SiO_2$) crystals. The true porosity of this glass-ceramic was 0.7%.

2. Densification and Crystallization Process of Glass Powder

The thermal shrinkage curve of the green glass powder compact of the composition 1+0.50F and DTA curve of the glass powders of the same composition are shown in Fig. 4. Crystalline phases, which were identified for the glass powders heated up to the various temperatures corresponding to the exothermal peaks of the DTA curves, are also shown in Fig. 4.

It can be seen from Fig. 4 that in the glass powders the apatite crystals precipitate first at about 870°C and then the wollastonite crystals at about 900°C, and that the densification of the glass powder compact starts at about 750°C, lower by about 90°C than the temperature where the apatite crystals begin to precipitate, and continues until the wollastonite crystals begin to precipitate at about 850°C. When the glass powders are heated up to temperatures above 1050°C, the apatite crystals disappear and whitlockite (β-$3CaO \cdot P_2O_5$) crystals precipitate at about 1100°C.

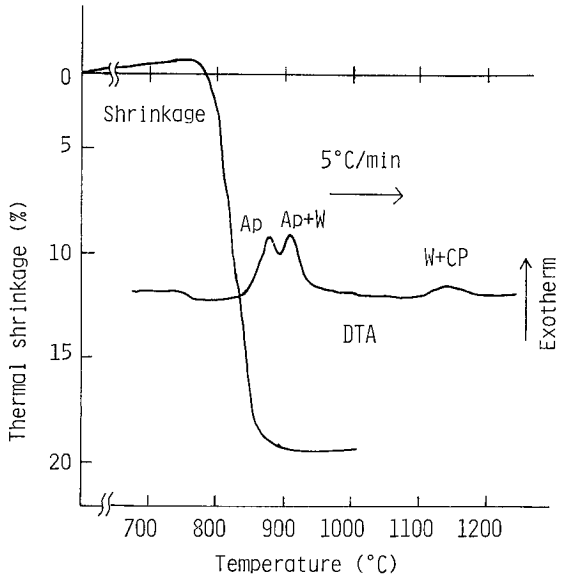

Fig. 4. Thermal shrinkage curve of the green glass powder compact and DTA curve of the glass powders. Composition: 1+0.50F. Ap: Apatite, W: Wollastonite, CP: Whitlockite.

3. Mechanical and Thermal Properties of Glass-Ceramic

The Young's modulus, Vickers hardness, bending strength, compressive strength and thermal expansion coefficient of the glass-ceramic 1+0.50F are given in Table III.

Table III. Mechanical and thermal properties of glass-ceramic 1+0.50F

Young's modulus	Vickers hardness	Bending strength	Compressive strength	Thermal expansion coefficient
103 GPa	7.16±0.84* GPa	157±8* MPa	1060±60* MPa	102×10^{-7}/K (40~980°C)

* standard deviation.

Although the mechanical strengths of the glasses hetherto known to form tight chemical bond with bones, e.g. Bioglass 45S5, are not reported, their bending strengths are speculated low, probably below 100 MPa. The bending strength of the apatite-containing glass-ceramic (Ceravital®) is reported to be 1000 kg/cm^2 (98 MPa) on most papers[2]. Those reported for the sintered dense hydroxyapatite ceramics are 113[5], 115[6] and 196[7] MPa. The last value is, however, that obtained for a small polished sample, and therefore, their practical value would be around 115 MPa. In comparison with these values, the bending strength of the present glass-ceramic, 157 MPa, is fairly higher. This value is, however, still a little lower than the highest value hitherto reported for human bone, 190 MPa[9].

The compressive strengths reported for the apatite-containing glass-ceramic (Ceravital®) and sintered dense hydroxyapatite ceramics are 500[4] and 510–920[7] MPa, respectively. In comparison with these values, the compressive strength of the present

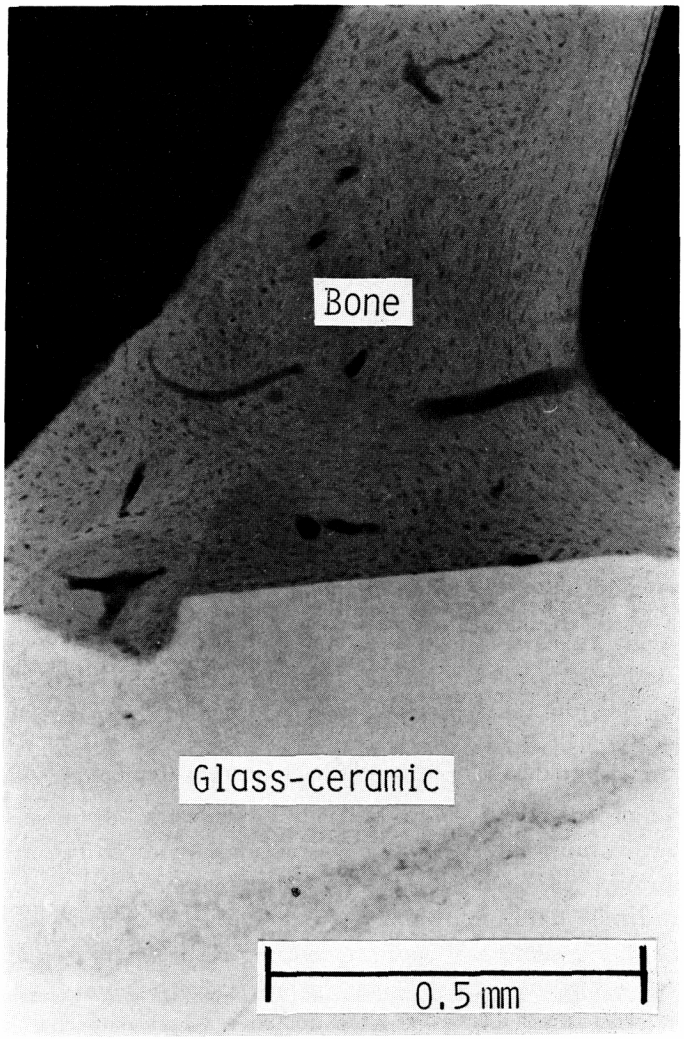

Fig. 5. Interface between glass-ceramic 1+0.50F and bone 25 weeks after implantation.

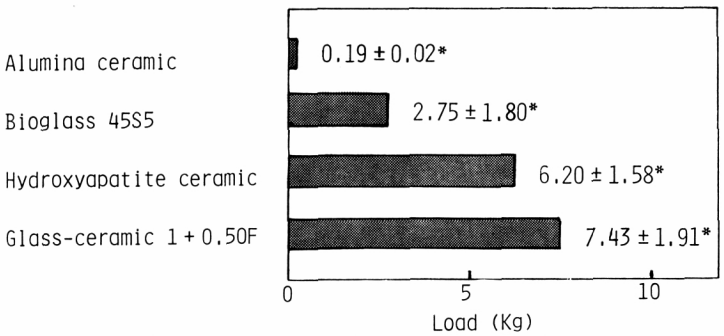

Fig. 6. Load necessary to cause fracture in pieces of the composites formed of implants and bones 8 weeks after implantation.
* Standard deviation.

glass-ceramic, 1060 MPa, is fairly higher. This value is much higher than the highest value hitherto reported for human bone, 230 MPa[9].

4. Biological Properties of Glass-Ceramic

The glass-ceramic 1+0.50F implanted in the rabbits showed good compatibility with the surrounding tissues without causing any foreign body reaction, even after 25 weeks. The good compatibility of this glass-ceramic with the bone is shown in Fig. 5.

The results of the fracture tests for the composites formed of the various implants and the bone are shown in Fig. 6. The tests were made for the composites excised 8 weeks after the implantation. The fracture occurred always at the interface between the implant and the bone for the alumina ceramic-bone composite, whereas it occurred at the interface between the implants and the bone or inside of the implants for the Bioglass-bone and hydroxyapatite ceramic-bone composites, and at the interface between the implant and bone or inside of the bone for the glass-ceramic 1+0.50F-bone composite.

It can be concluded from these results that the glass-ceramic 1+0.50F developed in the present study has a higher mechanical strength than the surrounding bone and shows the superior chemical bond with the bone, compared with the alumina ceramic.

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